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One-dimensional terahertz imaging of surfactant-stabilized dodecane-brine emulsions

by

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ABSTRACT

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Terahertz line-images of surfactant-stabilized dodecane($C_{12}H_{26}$)-brine emulsions are obtained by translating the emulsified region through the focus of a terahertz time-domain spectrometer, capturing a time-domain waveform at each vertical position. From these images, relative dodecane content, emulsion size, and stability can be extracted to evaluate the efficacy of the surfactant in solvating the dodecane. In addition, the images provide insight into the dynamics of concentrated emulsions after mixing.

Acknowledgements

Thanks to: The love of my life, Kristin, Daniel M. Mittleman, my advisor, Jonathan Laib, who began this project, and Reinaldo Navarrette, Paul Tortorici, and Jeremy Pearce for providing the surfactant-brine samples and insight into their behavior.

Contents

1. Introduction and background

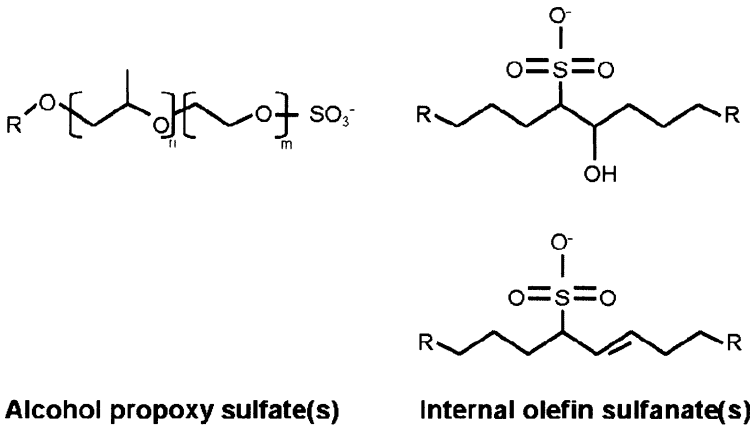
The understanding of emulsions and their dynamics are important to many industries, including the food[1], pharmaceutical[2], and petroleum industries[3]. Specifically, the petroleum industry is increasingly interested in the efficient extraction of petrochemicals from underground reservoirs, especially those reservoirs for which conventional extraction techniques have exhausted the easily mobilized oils. A variety of enhanced oil recovery (EOR) techniques have been developed, including those that rely on injection of gases, steam, and various liquid chemical mixtures to mobilize residual oil in a well[3]. In this latter case, surfactant-brine (salt water) mixtures are often employed. The surfactants can generate a sufficiently low oil-water interfacial tension to overcome capillary forces, to allow for the formation of an emulsion phase, and therefore to allow the emulsified oil to escape from porous rocks[4]. One challenge involves the choice of the surfactants since the chemical nature of the oil can vary from reservoir to reservoir. This choice depends on various factors including the salinity of the brine, ambient conditions, and the chemical nature of the oil. Selecting the correct surfactant can have a significant impact on the efficacy of residual oil extraction[5]. The ultimate goal is to maximize the oil content within the emulsion with the least amount of surfactant, which is essential for the extraction method to be cost-effective. Current methods for surfactant screening are qualitative and often rely on laboratory-based oil-water phase behavior tests. This involves visual inspection of the size of the micro-emulsion region after a 24 hour period. Unfortunately, the opacity of the oil phase makes it difficult to see the formation of the micro-emulsion phase[6] which hinders the ability to non-intrusively study their behavior.

Here it will be demonstrated that terahertz imaging can provide the quantitative data required to evaluate surfactants for EOR. The terahertz range is uniquely advantageous for studying the properties of these oil-brine emulsions as the oil phase is non-polar and therefore is relatively transparent. Previously terahertz spectroscopy has been used to study vibrational modes in nanometer-sized water-in-oil microemulsions[7,8]. More recently, spectroscopic measurements of emulsions with low water concentration have been performed using broadband[9] and single-frequency[10] terahertz sources. Extending these studies into the realm of terahertz imaging, vertical line-images can be used to investigate emulsions of higher water concentration and can provide a full profile of an emulsion, similar to the creaming or sedimentary profiles obtained through ultrasound techniques[11,12]. Moreover, the radiation can easily be focused to a spot size much smaller than the typical size (~cm) of a microemulsion region, so inhomogeneities within the micro-emulsion can be spatially resolved. Without prior knowledge of the constituent bulk oil phases' physical properties, the THz profiles can be used to determine oil content as well as the size and stability of the emulsion region, parameters which are of particular importance for EOR applications.

2. Surfactant-stabilized dodecane-brine emulsions

The surfactants (surface active agents) used in this study are a mixture of an internal olefin sulfonate (RSO_2O^-) and an alcohol propoxy sulphate ($ROSO_3$) (Fig 2.1), both which have previously been characterized for EOR applications and are therefore suitable for validating the terahertz imaging technique[6]. The amphiphilic nature of their molecular structure, being both hydrophobic and hydrophilic, allows them to solvate in

both water and organic liquids. This property allows the formation of micro-droplets, aggregates of the bulk oil or aqueous phase encapsulated by a surfactant monolayer, which are dispersed in a continuous phase of the other liquid.



Alcohol propoxy sulfate(s) **Internal olefin sulfanate(s)**

Fig 2.1 Molecular structures of the surfactants (Shell: EDORNET A771 and EDORNET O032) used to facilitate the formation of the dodecane-brine emulsions for validation of the THz imaging technique.

For the surfactants and brine salinities used in this experiment, mixing of the dodecane and brine/surfactant solutions results in a three phase system where the bulk brine, an emulsion of dodecane dispersed in brine and/or brine dispersed in dodecane, and bulk dodecane coexist in vertically stacked layers. Dodecane ($C_{12}H_{26}$) was used as the prototypical 'oil' in this initial experiment, since linear chain alkanes occur naturally in crude oil. The formed emulsion is a thermodynamically stable, macroscopically homogenous, and microscopically heterogeneous structure that scatters visible light (milky white layer in sample cell, Fig. 3.1.1). The size of the micro-droplets within the emulsion are much less than the THz wavelengths, so scattering may be ignored ($d<1\mu m$)[7]. For this experiment the free parameter is the salinity of the brine which alters the distribution of surfactant solvated between the aqueous and oil phases. At 'optimal'

salinity the surfactant will have the same affinity for both the oil and brine phase resulting in the highest concentration of surfactants at the brine-oil interface[14] which, in turn, maximizes the number of micro-droplets formed during mixing.

3. Terahertz imaging of dodecane-brine emulsions

3.1 Experimental setup

To obtain a series of vertical line-scan (one-dimensional) images of surfactant-stabilized emulsions over an extended period of time, the surfactant-brine solutions were mixed with dodecane (Acros Organics 99%+ purity) inside a custom designed z-cut quartz sample cell with a height of 14.5 cm and an internal path length of 1.10 mm. z-cut quartz was chosen for its transparency in both visible and terahertz wavelengths[14]. The sample cell is then translated vertically in the focus of a THz beam from a conventional time-domain spectrometer in a transmission configuration (Fig. 3.1.1). The spectrometer is a commercially available Picometrix T-Ray 4000 with 100Hz scan rate and a maximum bandwidth of 2 THz in this configuration.

The collimated beam from the spectrometer is focused and re-collimated using two PTFE lens in a con-focal geometry. Time-domain waveforms are measured at each of the vertical positions, forming a line-scan profile of the emulsified region. The fast acquisition time of the spectrometer coupled with the translation time of the sample cell allows measurement of a complete vertical profile in approximately 40 seconds depending on the signal averaging and the size of the region.

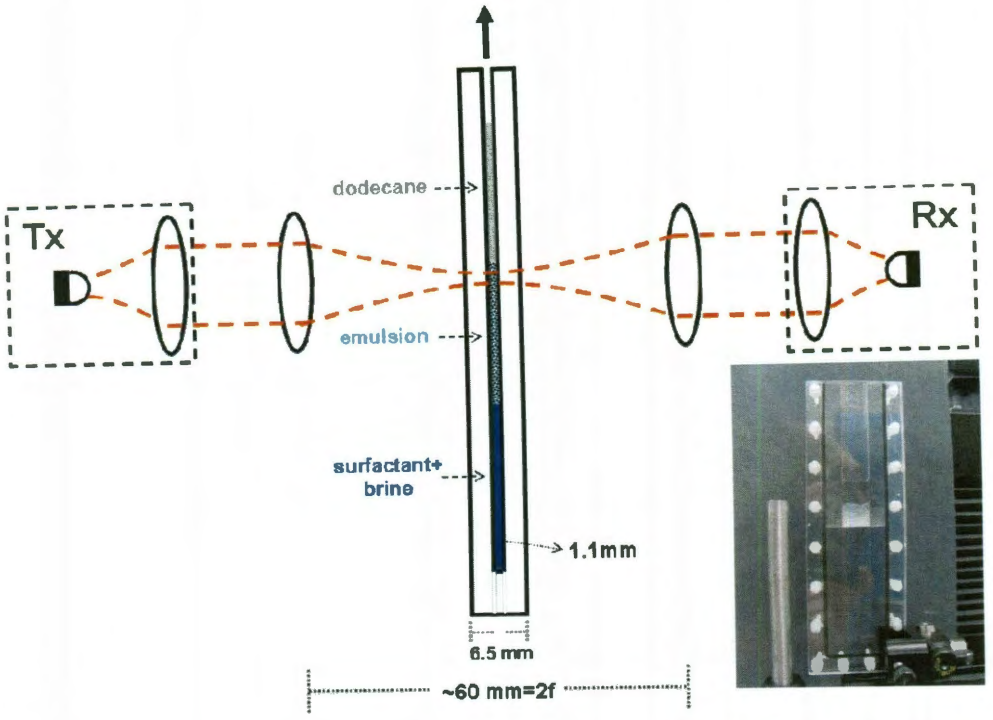


Fig. 3.1.1. The experimental setup consisting of a commercial THz-TDS spectrometer in transmission geometry, two PTFE lens, and a quartz sample cell which is translated vertically though the focal plane of the lenses. Inset photo is the quartz sample cell filled with dodecane (top layer), the surfactant/dodecane/brine emulsion (white layer), and brine (bottom layer), 24 hours after mixing.

3.2 Spatial resolution

To measure the spatial resolution of the spectrometer, an immiscible mixture of water and dodecane was placed in the sample cell, forming a sharp interfacial layer between the bulk aqueous and oil phases. Plotted in Fig. 3.2.1 are the averaged time-domain waveforms transmitted through the both components and their Fourier transforms. The H_20 signal was attenuated so strongly at this path length that an average of 100,000 waveforms was required to differentiate the signal from the background noise. Unfortunately, this almost complete attenuation of the signal through the aqueous phase prevents imaging across the emulsified region-aqueous phase boundary and subsequent calculation of the absolute ratios of the constituent parts of the emulsion. However, this

does not prevent the extraction of useful quantitative information from the images of the remainder of the emulsion.

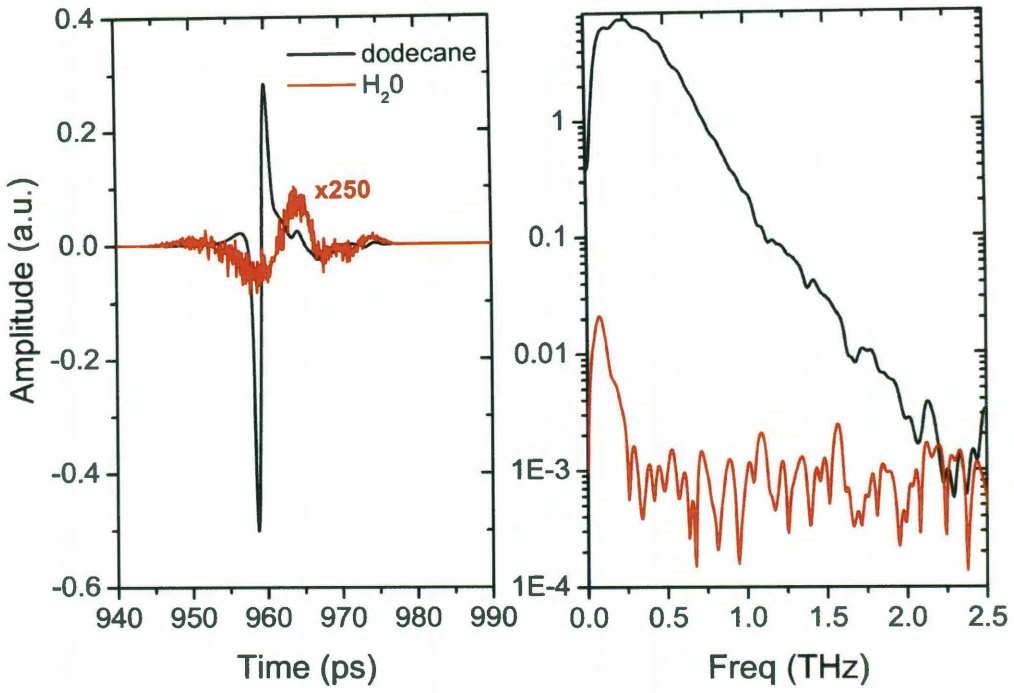


Fig. 3.2.1. The windowed time-domain waveforms and fourier transforms of the THz signals transmitted through the dodecane (black) and water (red). The time-domain waveform transmitted through the water has been multiplied by 250 and required extensive averaging to acquire.

The sample cell was translated vertically over the whole region, from the opaque water to the transparent dodecane, capturing a time-domain waveform every 250μm. For this spectrometer and the con-focal geometry, the focused terahertz beam diameter is strongly frequency dependent[15] which can be utilized to improve the spatial resolution of the image. Plotting the spectral amplitude at 650 GHz as a function of the vertical position creates the one-dimensional vertical profile of the system. This profile, plotted in Fig. 3.2.2, is effectively the edge-response function for this imaging system since the

dodecane-water interfacial layer width, the 'edge', is on the order of the diameter of a water molecule[16]. The frequency of 650GHz was chosen for optimal spatial resolution and to avoid THz water vapor absorption lines. To estimate the spatial resolution, the profile is fitted with a Boltzmann sigmoid function to determine the vertical positions corresponding to 10% and 90% spectral amplitudes. The difference in the vertical positions, Δy, is 0.65 mm, which is approximately 1.5λ, the estimated spatial resolution at 650 GHz.

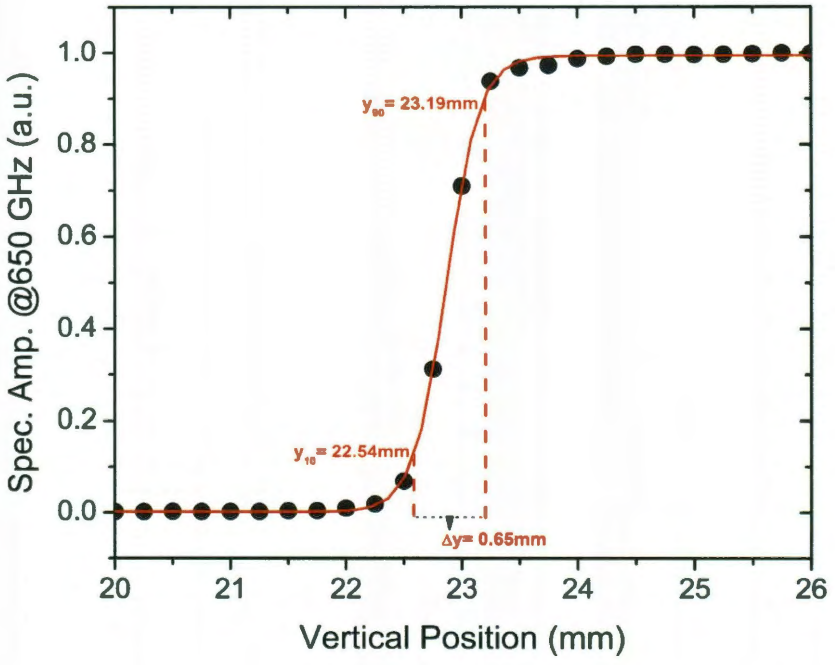


Fig. 3.2.2. The spectral amplitudes @ 650 GHz vs. vertical position for the water-dodecane system. This is effectively the edge-response function for the imaging system since the dodecane-water interface forms a sharp interfacial layer.

3.3 Imaging of the emulsions

In order to capture the time evolution of the emulsions, vertical scans were repeated every 15 to 30 minutes for 6 hours after mixing to investigate the evolution of

the emulsions' profiles and again after 24 hours to investigate their long-term stability. This procedure was repeated for each brine salinity, with NaCl concentrations ranging from 1% to 6% by weight. The surfactant concentration was constant across all the samples (2% by weight).

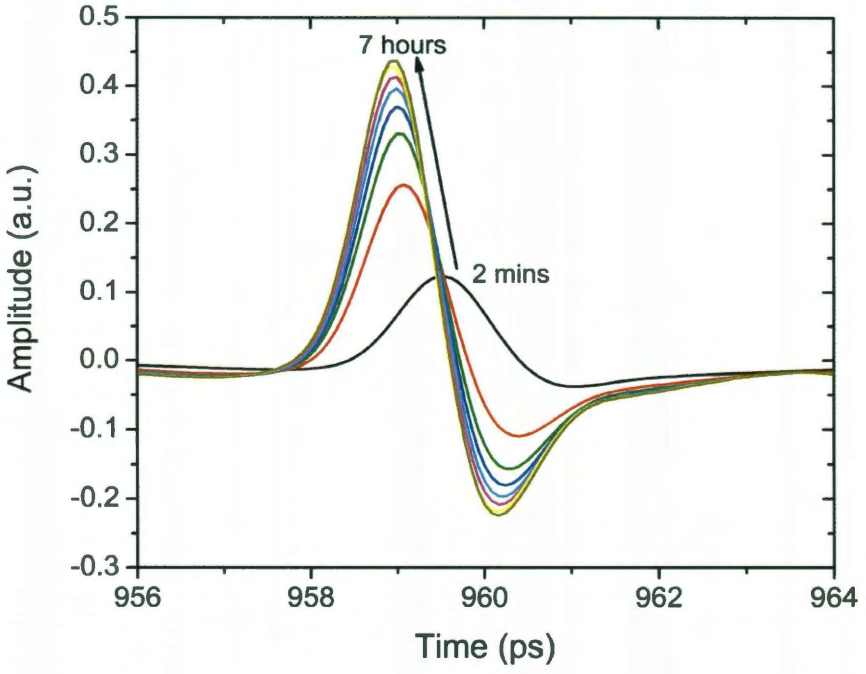


Fig. 3.3.1. Time-domain waveforms at a fixed vertical position (center of the emulsified region) for the 3% salinity dodecane-brine emulsion. The lowest amplitude waveform corresponds to 2 minutes after mixing while the highest amplitude waveform corresponds to 7 hours after mixing.

Fig. 3.3.1 shows typical waveforms obtained during the imaging scans for a fixed vertical position in the center of an emulsified region. The time-domain waveforms are plotted in 1 hour intervals, from 2 minutes after mixing to 7 hours after mixing. These waveforms represent the typical behavior of the measured waveforms at a fixed position

over time. The change in the peak to peak amplitude with time is indicative of a decrease in water concentration in the region illuminated by the THz beam.

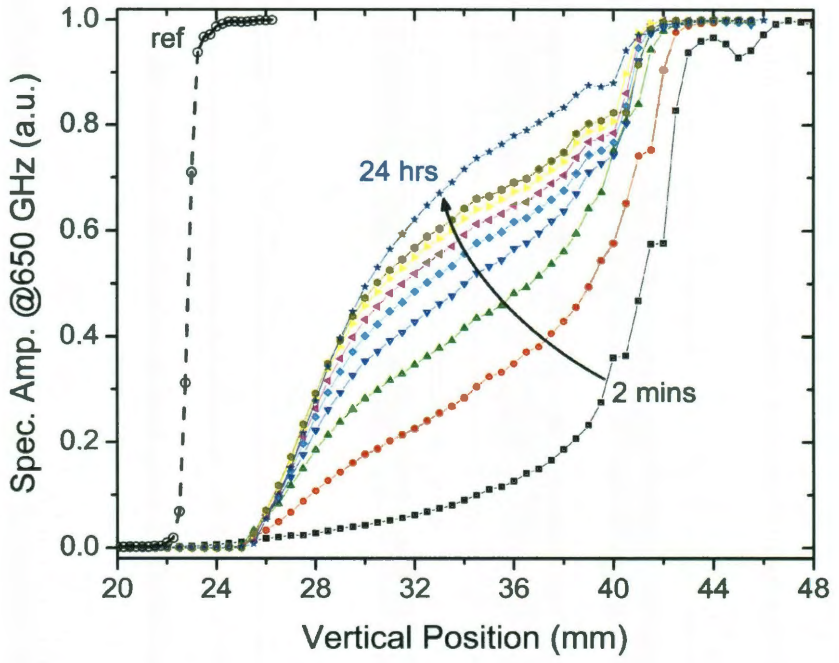


Fig. 3.3.2 Normalized spectral amplitudes plotted as a function of vertical position for the 3% salinity dodecane-brine emulsion. A profile was captured every hour for 7 hours and a final profile was captured after 24 hours. For reference, the dashed profile is the water-dodecane system used in the spatial resolution measurement.

Figure 3.3.2 illustrates the typical vertical profiles, specifically for the 3% salinity dodecane-brine emulsion, obtained over the 24 hour period. A spectral amplitude of zero corresponds to pure brine solution whereas the maximum spectral amplitude corresponds to pure dodecane. This is a typical result for these surfactant/brine-dodecane mixtures, illustrating the time evolution of the emulsions. Initially after mixing, the THz signal is attenuated strongly throughout the emulsion due to a relatively homogenous distribution of dodecane and brine, resulting in the initial low spectral amplitudes of the first profile. Due to the difference in density of the dodecane and brine, the larger micro-droplets will

aggregate toward the top or bottom of the emulsion (dependent on the identity of the dispersed phase) resulting in the curvature evident in the subsequent profiles. The varying micro-droplet sizes may be a result of the mixing process and/or coalescence of the micro-droplets after mixing. Despite the fact that the THz beam attenuation is essentially only affected by the concentration of the aqueous phase (since $\alpha_{brine} >> \alpha_{oil}$), no conclusions can be made about the identity of the dispersed phase. The change in contour of the profile could indicate either the brine, in the dispersed phase, is aggregating towards the bottom of the emulsion or the dodecane, in the dispersed phase, is aggregating toward the top of the emulsion, displacing the continuous phase brine in the process.

For these profiles, the observed rates at which contours of constant spectral amplitude converge to their limiting values could in principle be used to obtain information about the size of micro-emulsion droplets and if coalescence or flocculation is occurring, which would be an indication of incorrectly chosen surfactants and/or salinity. Stoke's Law relates the terminal velocity of a spherical droplet in a liquid to its diameter, the viscosity of the continuous phase, and the difference in density between the two continuous phases. In a well-characterized emulsion with low droplet density, this would allow estimation of micro-droplet sizes and could indicate flocculation or coalescence of the micro-droplets similar to ultrasonic analysis methods used for concentrated emulsions[17]. However, this analysis would assume that there are no retarding effects from collisions between droplets or friction from displaced fluid in the emulsified region and the sample cell walls. These assumptions are probably false for these emulsions. In addition, the identities of the dispersed and continuous phases are not

known for this particular surfactant/oil system at this time, further complicating the analysis. Thus, an approach based on Stoke's Law is not likely to provide accurate information without more knowledge of the emulsion's properties.

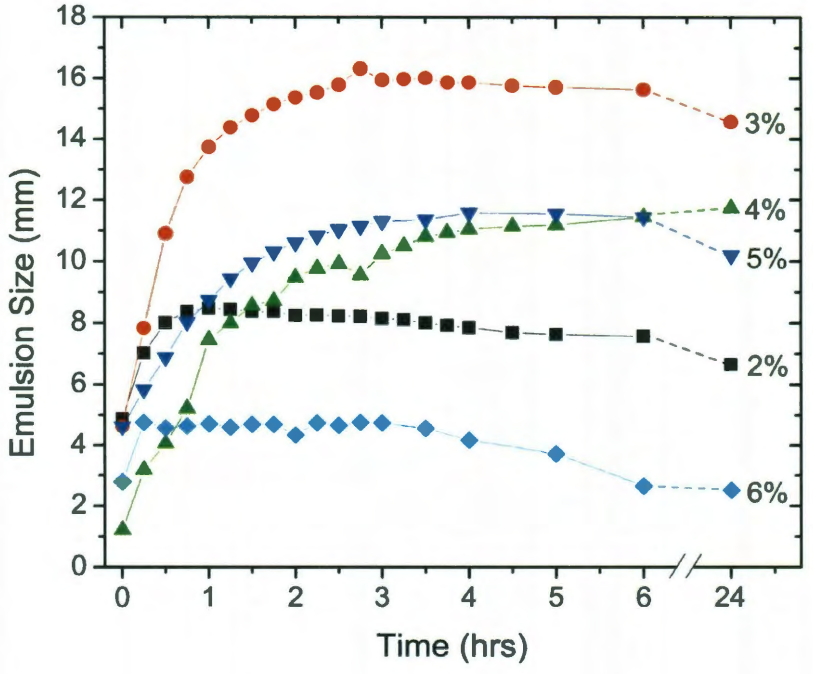


Fig. 3.3.3 The sizes of the emulsified regions, defined as the vertical distance between 90% and 10% spectral amplitude for each profile, plotted as a function of time for a few different emulsion salinities.

To compare the size of each emulsion, the vertical distance (Δy) between each profile's 90% and 10% spectral amplitude is plotted as function of time for several values of the salinity (Fig. 3.3.3). In contrast to the sharp interfacial layer of the water-dodecane system, the emulsions' profiles are not analytic functions of the vertical positions. Hence, interpolation was necessary in order to estimate the y_{10} and y_{90} positions. From this data and using the standard method of evaluating the effectiveness of these surfactants for EOR, the 3% salinity brine emulsion is considered the optimal salinity as it produces the

largest stable emulsion 24 hours after mixing. Over the course of 24 hours the 3% and 5% brine salinity emulsions remain relatively stable with a slight decrease in size while the 2% and 6% emulsions both decrease in size at a faster rate. The 4% emulsion slightly increases in size which may indicate better long term stability compared to the 'optimal' 3% salinity emulsion.

In the limit that the THz absorption of the brine is far larger than that of dodecane[18], the spectral amplitudes at each vertical position are proportional to the relative dodecane/brine ratio. Integrating the profiles over the emulsified region and normalizing to the value for the 3% brine salinity emulsion gives the total relative dodecane/brine ratio for each emulsion. These ratios are plotted as a function of time in figure 3.3.4. The time dependent ratios indicate the 3% and 5% emulsions may be absorbing dodecane well after mixing, even with the slight decrease in size, while the 4% emulsion's ratio increases at a faster rate, presumably correlated with its increasing size. The 2% and 6% salinity emulsions' dodecane/brine ratios decrease slowly over the 24 hour period.

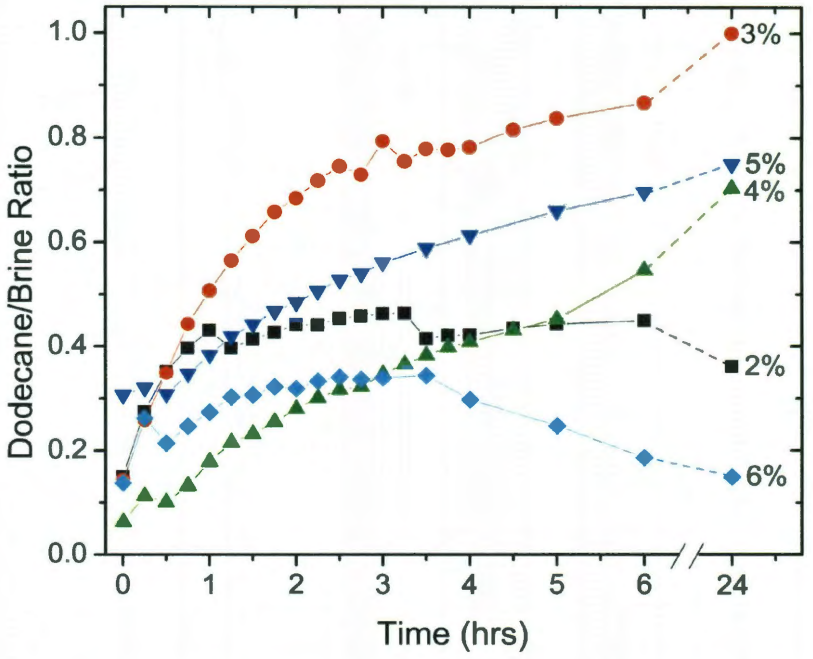


Fig. 3.3.4 Dodecane-brine ratios, normalized to the final 3% salinity emulsion dodecane-brine ratio, plotted as a function of time. The 3%, 4%, and 5% salinity emulsions continue to solvate dodecane after mixing. The 2% and 6% salinity emulsions' dodecane-brine ratios decrease after mixing.

The final ratios after 24 hours for each of the brine salinities reveal the optimal salinity for maximum dodecane content (Fig. 3.3.5), a valuable quantitative metric for EOR applications. In some cases, due to insufficient mixing and the small path length of the sample cell, large bubbles are formed in the emulsions which may eventually collapse or remain adhered to the boundaries of the sample cell, skewing the results. The samples with large visible inhomogeneities (circled data points in Fig. 3.3.5 and profiles in Fig. 3.3.6) were re-mixed resulting in homogenous emulsions. Hence, these inhomogeneities can be eliminated with a more robust mixing process and/or a larger sample cell size, assuming the surfactants and brine salinities have been correctly matched. If large inhomogeneities are consistently produced after repeated thorough mixing, this would be

a strong indication of a non-optimal surfactant-brine mixture such that THz imaging would not even be necessary.

The presence of impurities in the formation and behavior of these emulsions has not been tested. However, as long as the impurities are non-polar ($\alpha_{brine} >> \alpha_{oil+impurities}$), the impurities will only effect the value of the optimal salinity and the choice of surfactants and their concentration, values which can be revealed empirically using this technique.

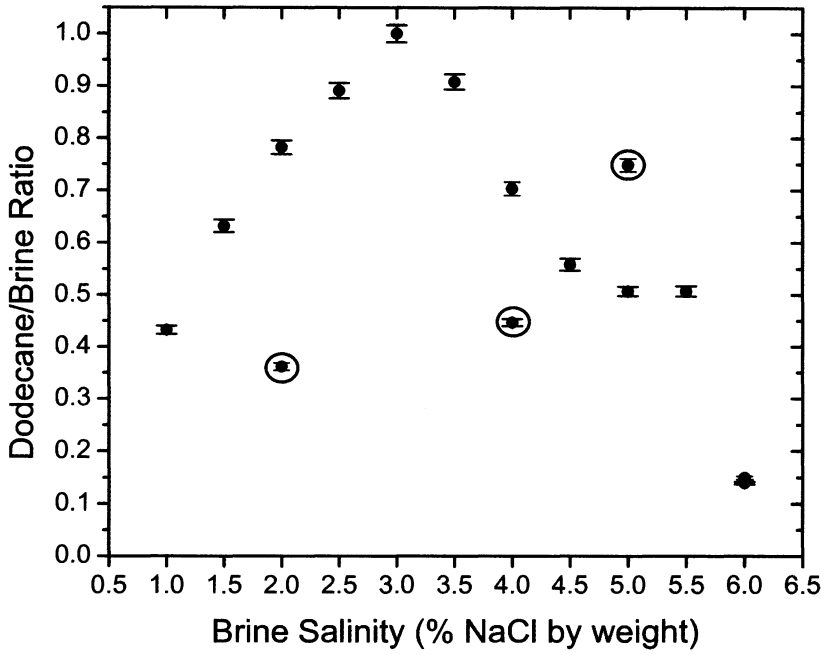


Fig. 3.3.5 The final (24 hour) dodecane-brine ratios revealing the optimal salinity for solvating the maximum amount of dodecane given the choice of surfactants and conditions. The circled data points indicate the cases where visible inhomogeneities skewed the results. The estimated error is propagated from the uncertainty in translation stage position (±5μm).

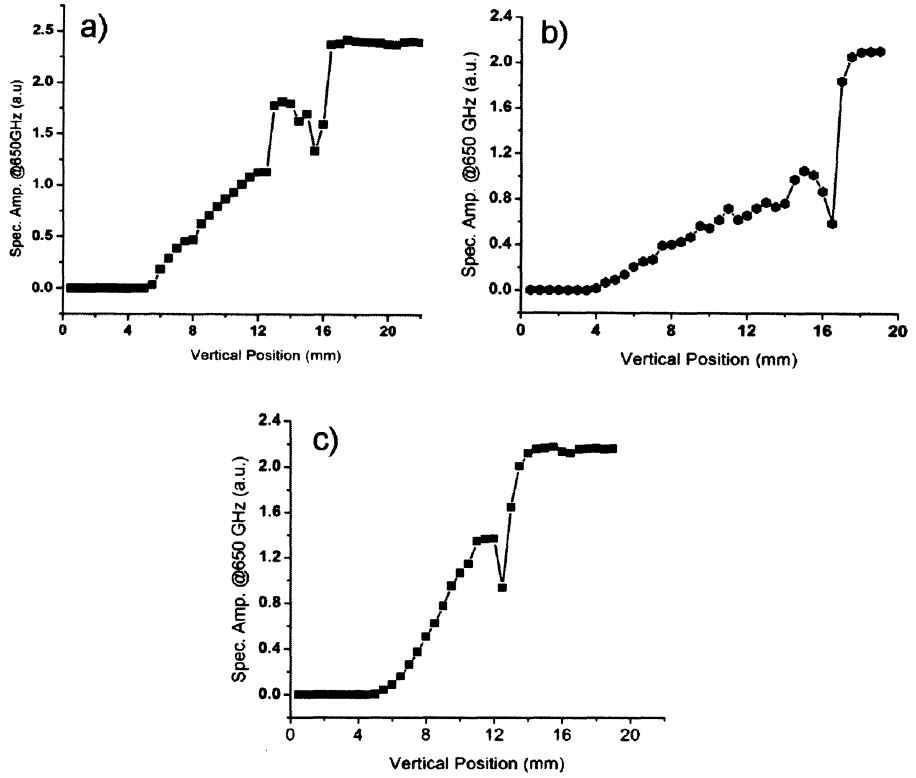


Fig. 3.3.6 Examples of the final 24hr 650GHz vertical profiles where inhomogenities, primarily macroscopic micelles adhering to the sample cell walls, skewed the results. a) 5% b) 2% c) 4% brine salinity emulsion profiles after 24 hrs.

4. Discussion and future work

Terahertz vertical line-scan images have been shown to effectively quantify the relative dodecane-brine ratios in emulsions of varying salinity, the parameter most important for determining the effectiveness of surfactant-brine solutions for EOR. In addition, and especially if the oil phase is opaque in the visible range, the ability to image the emulsions over time allows non-intrusive study of their dynamics including the evolution of the size and the relative ratios of their constituent parts, where previous industry standard visible range methods were inadequate. Hence, it has been demonstrated that THz imaging provides a robust quantitative metric for evaluating the efficacy of surfactants for EOR, without prior knowledge of the properties of the bulk oil

phase. In addition, the potential exists for this technique to be expanded to other industrial or research applications involving bulk aqueous and oil phase emulsions.

While the current imaging system achieves the desired goal of evaluating surfactant solutions for EOR, the ideal THz emulsion imaging system would be able to quantify the indices and absorption coefficients of the two immiscible liquid phases and, in turn, use this information for analysis of the intermediate emulsified phase. In the future, one significant change will be made to address the complete attenuation of the THz signal through the aqueous phase. Decreasing the sample cell path length will increase the likelihood of the formation and adherence of inhomogeneities to the sample cell walls so it is not an option. Instead the imaging setup will be changed to reflection geometry where the Fresnel reflection from the inner surface of the sample cell, the cell-emulsion interface, can be used as the signal and the air-cell interface can be used as a reference[19]. In addition, the reflection from the back of the sample cell can be used as a double-pass transmission measurement. This will increase the versatility of the emulsion imaging system, as both the index and absorption for the highly absorbing phases can be measured using this emulsion imaging technique; expanding its use beyond just surfactant evaluation for EOR.

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